SPECTRAL EMISSION CHARACTERISTICS OF SIZE-GRADED COAL PARTICLES*

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The spectral emission characteristics of coal are examined using Fourier transform infrared emission spectroscopy. The data were collected from a single layer of stationary, narrowly size-classified samples of coal and graphite placed on a heated NaCl window. Sample temperatures ranged from 120 to 200°C. FTIR data were collected at wavelengths between 2.2 and 17 μm (between 4500 and 580 cm^{-1}). Particle sizes ranged from 40 to 120 μm and coal rank ranged from lignite to bituminous.

The focus of this work is to evaluate the effects of the nongray emission characteristics of coal on heat transfer calculations and pyrometry measurements. Chemical functional groups responsible for the features of the spectral emission are identified but not discussed. Well characterized spectral features from coal samples are observed and discussed. The intensity of spectral peaks due to chemical functional groups in coal are analyzed as a function of particle size and extent of reaction. The impact of spectral irregularities on pyrometry measurements and heat transfer calculations is evaluated. Featureless regions of the infrared emission spectra of coal are also analyzed and compared to graybody behavior. Reliability of pyrometry measurements in these regions and effective emissivities of coal particles for heat transfer calculations are discussed.

INTRODUCTION

Spectral and total emission characteristics of coal have been reported in the past, with emissivities ranging from 0.1 to near unity. Several investigators (1-3) have published results indicating that coal is not a strong absorber of radiation at infrared wavelengths. Values of the imaginary part of the complex index of refraction on the order of 0.05 are reported by these authors. Other authors report much larger imaginary coefficients, of the order of 0.3 (4-6), indicative of higher abosrbance and emittance of radiation.

A strong and irregular dependence of emissivity on wavelength would be expected of an organic compound containing a variety of chemical functional groups, such as coal, if the material is either generally transparent or very thin. Such results are reported by Solomon and coworkers (3) for particles less than 40 μm in diameter, although the size of the particles is not always well defined in their work. Commonly available infrared absorption and diffuse reflectance spectra of coal samples are consistent with the spectral features reported by Solomon. However, these features should become indistinguishable from the diffuse background absorption as the particle size increases. Solomon noted this trend, but did not define a particle size where the spectral features of the emission become insignificant compared to the diffuse background radiation. Large or highly absorbing particles should show less variation of emissivity with wavelength; they should become approximate gray-bodies.

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The overall emissivity of coal includes diffuse, broadband absorption in addition to peaks associated with specific functional groups. The broadband absorption of coal probably arises from electronic excitations of π electrons in the graphitic, aromatic bonds in the coal matrix (7-9). These electrons are loosely bound by the nuclei, and can absorb radiation over a continuous wavelength region which extends far into the infrared. However, the electrons are not entirely free from nuclear attractions, and their emission spectra would not necessarily be expected to follow Planck's law. Therefore, even the radiation from coal at wavelengths void of any identifiable functional groups may not be gray in its characteristics.

The literature cited above indicates that the spectral emission of coal particles at sizes of importance to pulverized coal combustors (50-150 μm) is potentially nongray and could depend in complicated ways on particle size, coal rank, temperature and extent of reaction. However, the emission would be expected to behave more like a graybody with increasing particle size, coal rank, temperature, and extent of reaction. Although all of the literature suggests that there is some size at which the coal particle emission is nongray, no study has been sufficiently definitive to quantify such a size for coals of various rank.

IMPACT OF NONGRAY COAL EMISSION ON COMBUSTION

The potentially nongray emission of coal particles impacts combustion in the areas of overall heat transfer and in the calculation of particle temperature from pyrometer measurements. An abnormally low emissivity due to nongray behavior could impact radiative heat transfer effects and either increase or decrease the rate of particle heat up, depending on the wall and particle temperatures and the optical depth of the combustion gases. Data collected in experimental and industrial combustors in which radiation is a signficiant contributor to the overall heat transfer to the particle may be subject to misinterpretation or error if an inappropriate emission spectrum is assumed. A particle emissivity which depends on particle size, coal type, and extent of burnout may be required to accurately calculate radiation heat transfer.

The sensitivity of two-color pyrometry to nongray emissions is illustrated in Figure 1 for three sets of wavelengths. The effective emissivities of the coal were assumed to be 0.9 and 0.8 at λ_1 and λ_2, respectively. The same results would apply for any emissivities with a ratio of 9:8. Pyrometry measurements at longer wavelengths are more sensitive to nongray emissivities. For example, if the ratios of emissivities are 9:8, a pyrometer operating at 5 and 6 μm would indicate the temperature of a 1500 K particle is over 3000 K and that a 2000 K particle would be measured as over 9000 K. This sensitivity provides practical motivation for determining the spectral emissivities of coal.

The experimental work reported in this paper analyzes spectral emissivities of various sizes and ranks of coal particles using emission FTIR techniques. Discussions of the experiment, the functional groups found in the spectra, and the size, burnout, and rank dependence of the findings follow.

EXPERIMENTAL PROCEDURE

Figure 2 is an illustration of the experimental equipment and optical layout employed in this study. A single layer of sized particles of coal and graphite were placed on a horizontal window of NaCl mounted in an aluminum ring. An electric strip heater was wrapped around the mount. The NaCl window was used because it can withstand higher temperatures without degradation and has a higher thermal conductivity than other windows that are transparent throughout the infrared spectrum. Temperatures as high as 400°C are possible

with this arrangement, although the temperatures used to obtain the spectra presented in this report seldom exceeded 200°C. The heated sample, optics, interferometer, and detector were enclosed in a nitrogen-purged container.

All coal samples were obtained from the Pennsylvania State University Coal Bank. The coal samples were ground in a nitrogen atmosphere, size classified by sieve trays, and some were dried in a nearly inert atmosphere at 305°C. Graphite samples were prepared similarly. All samples were visually examined and some were photographed after they were placed on the window to ensure they were well size-classified and formed a single layer.

The heated sample disc was movable in the horizontal plane, allowing the FTIR instrument to measure emission from the coal and from the graphite through the heated window, and from the heated window itself. The field of view of the system, calculated from geometric optics, was 6 mm in diameter at the sample plane. In practice, a portion of the signal from the edge of the collecting lens was lost, probably due to overfilling the detector.

The spectra in this paper were produced by averaging 800 interferograms, each with a resolution of 4 cm^{-1}. Approximately 5 minutes were required to obtain one spectrum under these condtiions. The large number of scans produced a high signal-to-noise ratio over most of the infrared region; peaks were observed with sufficient resolution to allow comparison with literature results. The emissivity of the coal (ϵ_s) was determined at each wavelength from the following equation:

$$\epsilon_s = \left(\frac{R_s/A_s - R_w/A_w}{R_g/A_g - R_w/A_w} \right) \epsilon_g \qquad 1)$$

where R is the measured intensity (radiance and system response), A is the emitting area, ϵ is emissivity, and subscripts s, g, and w refer to sample (coal), graphite, and window, respectively. The numerator in Equation 1 represents the energy flux emitted by the sample, accounting for background emission from the window. The quantity in parenthesis represents the emissivity of the sample relative to the emissivity of the graphite, and hence the right-hand side is multiplied by ϵ_g. This approach assumes that ϵ_g is constant over the wavelength spectrum. The spectral emissivity of the graphite particles was determined by correcting the measured intensity (R_g) for the system responsivity; the graphite particles exhibit nearly graybody behavior with a total emissivity of 0.92.

Emission FTIR is subject to interference from atmospheric absorption and emission. This effect was minimized in this experiment by measuring the emissivity of a reference body (graphite) of the same size and under the same conditions as the coal. This experimental procedure is roughly equivalent to individually calibrating the system responsivity for each measurement. Our experience was that this technique, combined with Equation 1, yielded spectra of superior quality to the more common approach of determining a single fixed system responsivity for several or all of the spectra.

The emitting areas of the graphite and coal and the transmissivity of the window were determined by measuring the extinction of a HeNe laser beam as it passed through a sample. The HeNe beam was expanded, and a central portion of the beam with the same diameter as the diagnostic area (6 mm) was used to minimize

errors from gradients in beam intensity. A power meter with a large detection area was used to measure the beam intensities and minimize errors due to scattered light.

The particle temperatures were assumed to be close to the window temperature, which were measured with a type K thermocouple placed on the window itself in the vicinity of the sample. The temperature at the center of the window was typically 5-10 Kelvins lower than that at the edge. However, the samples were located equidistant from the window edge to minimize errors due to temperature gradients. The data analysis can be completed without specifying the actual temperature so long as the window, coal, and graphite temperatures are equal.

The estimated accuracy of the measured emissivities is $\pm$ 5 relative percent. The major source of uncertainty in the emissivity was the determination of the actual emitting surface area. Although the HeNe laser could accurately measure the cross-sectional area of the samples within the nominal 6 mm sample, there were indications that a fraction of the signal from this area was not transmitted to the detector.

FEATURES OF THE COAL SPECTRA

Figure 3 is typical of the spectra collected in this study, showing the spectral emissivity of 40 μm diameter particles of a hvA bituminous coal (Pittsburgh #8, PSOC 1451). Peaks from various functional groups are identified in the figure. One small peak, at about 1850 cm^{-1}, is not typical of coal and has not yet been identified. The remaining peaks agree precisely with published spectra collected with a variety of instruments and techniques and validate the experimental procedure described above. Similar spectral features were found in the coals of other ranks. The spectra show maximum emissivities close to unity in regions of functional group absorption. The absorption of these peaks is typically high for submicron particles (8) and should not decrease with increasing particle diameter.

Some reaction of the coal was observed when the temperature was held above 150°C for 3 hours or longer. For example, the evolution of a peak at 1850 cm^{-1} is observed over a 2.0 hour period. Other coal reactions which were indicated by reductions in peak size include loss of hydrogen-bound hydroxyl and a small decrease in the aliphatic carbon. However, consecutive spectra taken within one hour of each other showed no losses and were reproducible at temperatures below 170°C. In any case, there was no evidence that a spectrum changed during the 5 minutes required to collect it.

DEPENDENCE OF EMISSIVITY ON SIZE, BURNOUT AND RANK

The spectral emissivity for 115 μm particles of a Pittsburgh seam (high-volatile A) bituminous coal is shown in Figure 4. A comparison of Figures 3-4 shows the dependence of spectral emissivity on coal particle size. The peaks are broader, the valleys are higher, and the emissivity in the featureless regions has increased for the larger particles, as anticipated. The emissivity of 115 μm particles of this bituminous coal varies from 0.7 to 1.0 over the range of 500 to 4100 cm^{-1}.

The spectral emissivities for 115 μm particles of a subbituminous coal and a lignite are shown in Figures 6 and 7. The subbituminous sample (PSOC-1445d) is a Western coal from the Blue #1 seam, and the lignite sample (PSOC-1507d) is a lignite from the Beulah Zap seam. These coal samples were sieved and aerodynamically classified under nitrogen to enhance size classification. These particular samples were not dried prior to analysis.

The dependence of emissivity on coal rank can be seen by comparing Figures 5-7. The nongray behavior of the lignite is more pronounced than in either of the higher rank coals, with emissivity varying from 0.57 to 1 0 in the region of the infrared indicated. However, little indication of aromatic spectral features is present in either of these samples. Interference from water in these undried samples is evident in the spectra.

A spectrum of partially devolatilized bituminous (PSOC 1451) coal appears in Figure 8. This sample was prepared by entraining the coal in a 1000 K inert gas stream in a down-fired, laminar flow reactor. The proximate volatile content of the parent coal is 40 % on a dry, ash-free basis. The weight loss of these samples has not yet been measured, but it is estimated that devolatilization was nearly completed when the sample was collected. The unreacted coal particles used in this analysis were those used to generate Figure 5. The dependence of particle emissivity on coal burnout can be seen by comparing Figures 5 and 8.

The emissivity of these particles is quite constant at 0.8 at wavenumbers above 1900 cm^{-1}. The aliphatic and hydroxyl groups, which were emitting strongly in the unreacting coal, appear to have either volatilized or reacted to form other compounds. However, a weak aromatic peak persists at 3000 cm^{-1}. The emissivity of the aromatic peaks between 500 cm^{-1} and 1900 cm^{-1} slightly exceeds that of the parent coal, possibly due to the formation of tar. Finally, the emissivity in featureless regions of the spectrum did not change appreciably from the parent coal.

IMPLICATIONS ON PYROMETRY AND RADIATIVE HEAT TRANSFER

The spectral emissivity shown in Figure 5 can be used to evaluate the potential impact of nongray emissions on pyrometry measurements. For example, a two-color pyrometer operating at 3333 and 2500 cm^{-1} (3 and 4 μm) would overestimate the temperature of a 1500 K particle by 200 K. A similar error would occur if the pyrometer operates at 3333 and 2000 cm^{-1} (3 and 5 μm). If the pyrometer were operating at 2000 and 1667 cm^{-1} (5 and 6 μm), it would underestimate the particle temperature by 700 K. Errors in pyrometry measurements due to nongray emissivities can be minimized by making one measurement at a short wavelength (around 1 μm) or increasing the separation between wavelengths, the former strategy being more effective than the latter. These trends are shown in Figure 1. However, signal strengths at typical combustion temperatures decrease sharply with decreasing wavelength in the near infrared and visible regions, requiring a judicious choice between acceptable signal-to-noise ratios and sensitivity to this type of error.

Total emissivities for use in radiative heat transfer calculation will depend in a complicated way on coal rank and on particle size, temperature, and degree of burnout. For high rank coals above 40 μm in size, the total emissivity could vary between 0 65 and near 1.0. Lignites have a wider variation in emissivity. The importance of these variations and the effect they have on heating rate depend primarily on the combustor configuration and flow field. In many instances, devolatilization may be completed before the particle reaches a high temperature, and only the optical properties of the residual char affect combustion behavior.

CONCLUSIONS

An emission FTIR experimental technique is used to study emission characteristics of coal particles. Coal particles in the size ranges between 40 and 115 μm show nongray behavior at wavelengths between 2.2 and 17 μm Spectral emissivities of high rank coals vary from 0.7 to 0.98. Spectral emissivities of lignites may be as low as 0 5 at some wavelengths. The particles generally are more gray as particle size, rank and extent

of burnout increase. The emissivity generally increases with increasing rank and particle size. As burnout increases, the particle emissivity can either increase, decrease, or remain constant, depending on the region of the spectrum being considered.

Pyrometry measurements in the 2.2 to 17 μm wavelength interval are subject to errors due to nongray effects. The errors in temperature measurement vary from a few hundred degrees to many thousands, depending on the wavelengths chosen. Operating one channel of the pyrometer at a short wavelength reduces the chance for error.

The effect of nongray emissions on heat transfer calculations will depend on the particular combustor and flow field being used. Total particle emissivities range from about 0.6 to 0.95 for 115 μm diameter particles, depending on particle temperature and coal rank. Smaller particles from low rank coals have lower emissivities. Partially devolatilized samples of bituminous coal emit as gray bodies over a large portion of the infrared spectrum, with emissivities of about 0.8.

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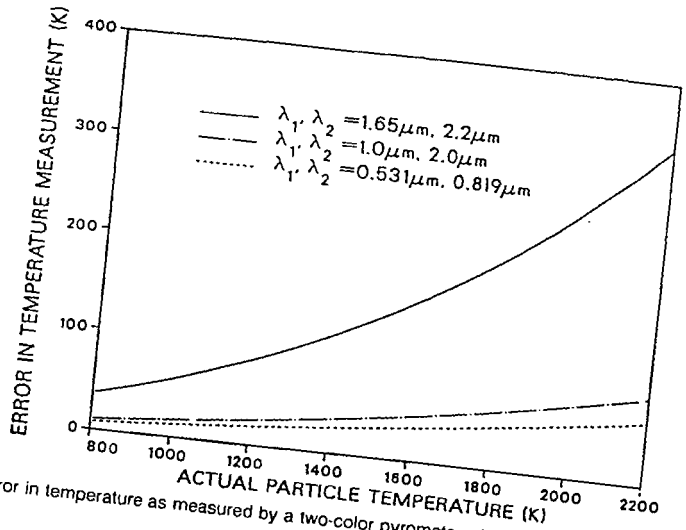

Figure 1. Error in temperature as measured by a two-color pyrometer when the emissivity ratio at λ_1 and λ_2 is 9·8.

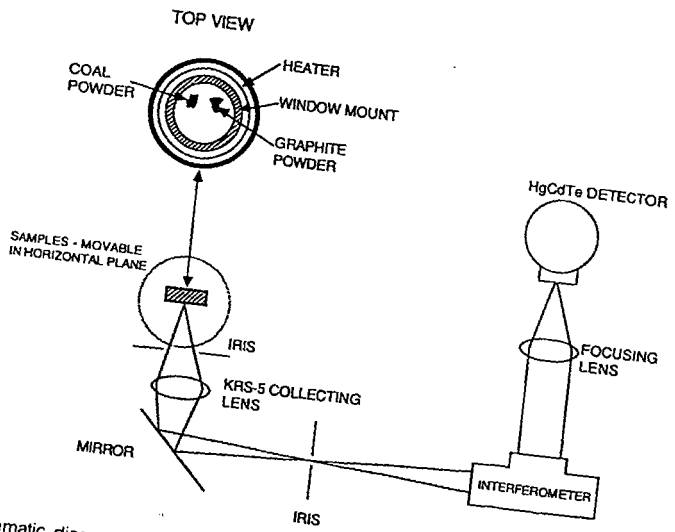

Figure 2. Schematic diagram of experimental facility for measurements of the spectral emissivity of coal particles.

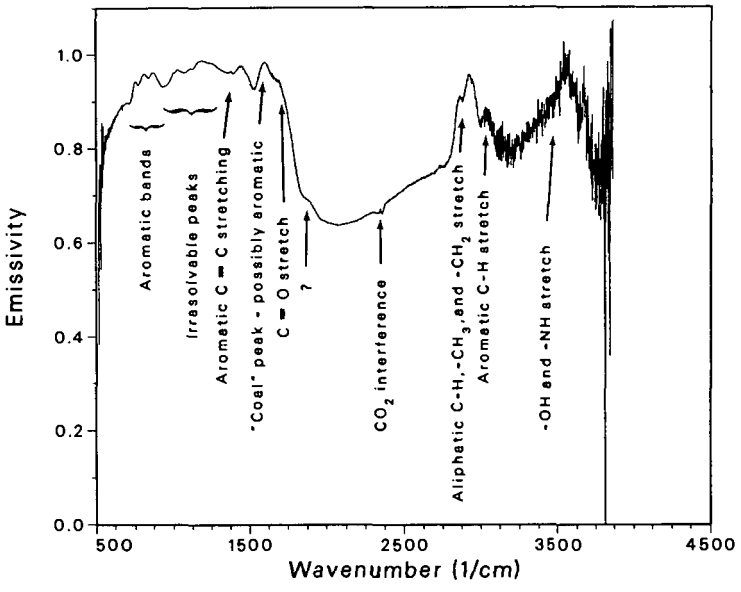

Figure 3. Spectral emissivity of 40 μm hvA bituminous coal (PSOC 1451) at 171°C, identifying peaks associated with various coal functional groups.

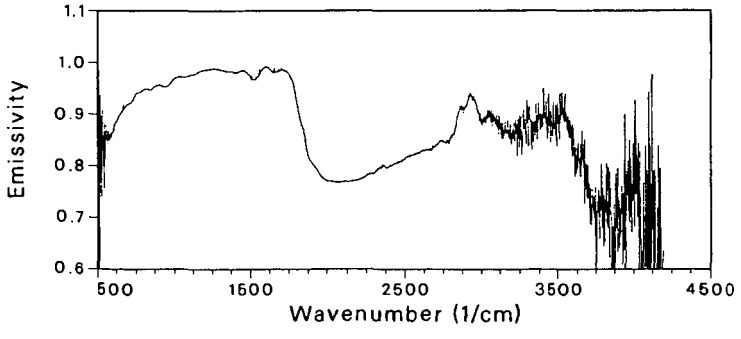

Figure 4. Spectral emissivity of 115 μm diameter hvA bituminous coal particles (PSOC 1451) at 182°C.

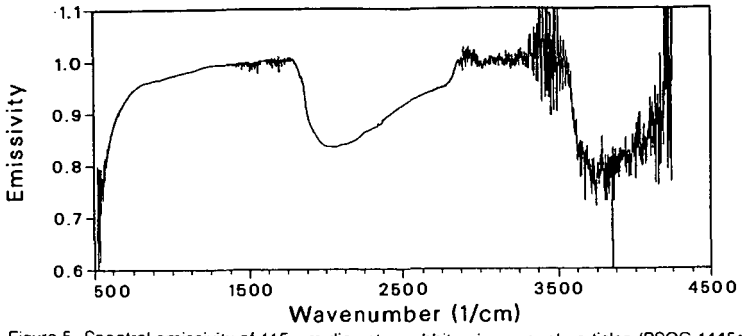

Figure 5. Spectral emissivity of 115 μm diameter subbituminous coal particles (PSOC 1445d) at 180°C.

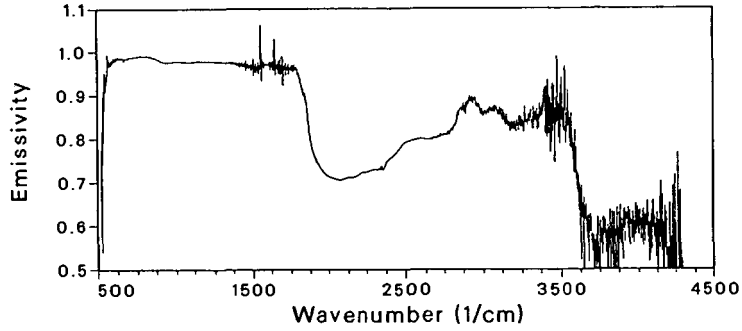

Figure 6. Spectral emissivity of 115 μm diameter lignite particles (PSOC 1507d) at 190°C.

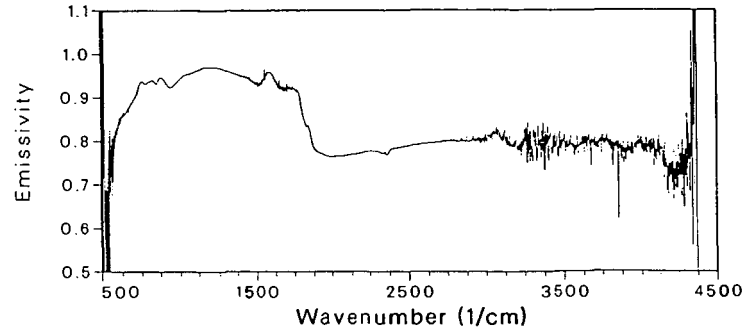

Figure 7. Spectral emissivity of 115 μm diameter hvA bituminous coal particles (PSOC 1451) at 182°C after partial devolatilization at 1000 K.